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**********************************02955**********************************

PAGE 1

LEVEL 2 - 1 OF 2 PATENTS

5,401,714

<=2> GET 1st DRAWING SHEET OF 1

Mar. 28, 1995

Field-effect device with a superconducting channel

INVENTOR: Chaudhari, Preveen, Briarcliff Manor, New York
Mueller, Carl A., Hedingen, Switzerland
Wolf, Hans P., Zurich, Switzerland

REF-CITED:
... OTHER PUBLICATIONS

F. Hebard et al. (1) "Experimental Considerations in the Quest for a in-Film Superconducting Field-Effect Transistor", IEEE Trans. on MAG. vol. 23, No. 2, Mar. 1987, pp. 1279-1282.
A. F. Hebard et al. (2) "Electric-Field Modulation of Low Electron Density Thin-Film Superconductors", Novel Superconductivity, Jun. 22-26, 1987, pp. 9-22.
A. T. Fiory et al. "Electron Mobility, Conductivity, and Superconductivity near the Metal-Insulator Transition", Phys. Rev. Lett. vol. 52, No. 23, 4 Jun. 1984, pp. 2057-2060.
P. Chaudhari et al. "Critical-Current Measurements in Epitaxial Films of YBa2Cu3O 7-x Compound" Phys. Rev. Lett. vol. 58, No. 25, 22 Jun. 1987.
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Clark et al. "Ion Beam Amorphization of YBa2Cu3O x " Appl. Phys Lett ...

... 100) SrTiO3 prepared by pulsed laser evaporation" Appl. Phys. Lett vol. 51, No. 11, Sep. 14, 1987 pp. 861-863.
C. W. Chu et. al. "Supercond. at 93oK in a new Mixed-Phase YBaCuO Comp. System at Ambient Pressure" Phys. Rev. Lett. 58, No. 9, Mar. 1987 pp. 908-910.

T:
... a substrate and comprising a channel with source and drain as well as a gate that is separated from the channel by an insulating layer. The channel is made of a high T c metal-oxide superconductor, e.g., YBaCuO, having a carrier density of about 10<21> /cm<3 > and a correlation length of about 0.2 nm. The channel thickness is preferrable in the order of 1 nm. The superconductor is preferably a single crystalline and oriented such that the superconducting behavior is strongest in the plane parallel to the substrate. With a signal of a few volts applied to the gate, the entire channel cross-section is depleted of charge carriers whereby the channel resistance can be switched between a "zero resistance" (undepleted, superconducting) state and "very high resistance" (depleted state).

SUM:
... field-effect device such as a field-effect transistor (FET) that can be utilized in electronic circuitry and that is suited for use in integrated circuits. The device comprises a layer of superconducting material forming the

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channel through which a current of charge carriers may flow, a pair of terminals for feeding a current through the channel, and a control gate for applying an

electric ...

... together with the fact that the resistance of metallic wiring or device connections decreases with decreasing temperature, make low temperature systems attractive.

Recording the development of low temperature devices, there have been proposals for semiconductor FET structures having superconductor source and drain electrodes and where the semiconductor current channel, due to the so-called "proximity effect", becomes superconducting in the vicinity of the superconductor electrodes. An article entitled "Three-Terminal Superconducting Devices", written by W. J. Gallagher (IEEE Trans. on Magnetics, Vol. MAG-21, No. 2, March 1985, pp. 709-716) provides a brief description of such proximity effect devices as well as prior art references. Fabrication and operating margins of these devices would, however, be rather critical.

Furthermore, there have been proposals for FET structures comprising a superconductor channel. They have been described, for example, in the following articles: "Superconducting Field-Effect Transistor" by F. F. Fang et al, (IBM Technical Disclosure Bulletin, Vol. 19, No. 4, September 1976, pp. 1461-1462), and in "Experimental Considerations in the Quest for a Thin-Film Superconducting Field-Effect Transistor" by A. F. Hebard et al (IEEE Trans. on Magnetics, Vol. MAG-23, No. 2, March 1987, pp. 1279-1282).

These articles describe studies on structures with a superconductor channel having a thickness of about 10 nm. An applied electric field causes a slight change in carrier density in a thin surface layer at the gate-superconductor interface. This change in carrier density in turn results in a shift in transition temperature T c in the thin layer. By applying signals to the gate, the thin layer can be switched between "superconducting" and "normal conducting" states. This results in a change in channel resistance.

Since the field-induced effect does not extend deeply into the channel material, various approaches to enhance the magnitude of the effect have been studied and published by A. T. Fiary and A. F. Hebard in two articles "Field-Effect and Electron Density Modulation of the Superconducting Transition in Composite In/InOx Thin Films" (Physica 135 B, 1985, pp. 124-127, North-Holland, Amsterdam) and "Electric Field Modulation of Low Electron Density Thin-Film Superconductors" (Proc. Internat. Workshop on Novel Mechanism of Superconductivity, Berkeley, June 1987). There is another article on this subject by M. Gurvitch et al, "Field Effect on Superconducting Surface Layers of SrTiO3" (Materials Research Society 1986, pp. 47-49).

The drawback of these "surface effect" devices is that the change in channel resistance is still quite small. Even in the "switched" thin surface layer the change is only from metal-conducting to superconducting and, in addition, the

03

bulk section of the channel that is not affected by the applied field acts as a metal-shunt. Therefore, the obtainable output signals are too small to be able to drive next stage FET ...

... present, the speed of integrated circuits is essentially determined and limited by the relatively high resistance of the wiring and device connections rather than by the devices themselves. Further progress could therefore be achieved if the wiring could be made of superconductor material. At operating temperatures below T c of the superconductor material, the line resistance

would be reduced to zero and systems with devices linked by resistance-free connections offer increased speed.

This has become feasible since the discovery of a new class of high T c metal-oxide superconductors (also referred to as ceramic superconductors) that were first described by G. Bednorz and K. A. Mueller in their article "Possible High T c Superconductivity in the Ba-La-Cu-O System" (Z. Physics, Condensed Matter, Vol. 64, 1986, pp. 189-193). Further developments have resulted in metal-oxide superconductor materials, such as YBaCuO and others, having a T c well above the temperature of liquid nitrogen. One such composition has been described by C. W. Chu et al in an article "Superconductivity at 93K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure" (Phys. Rev. Lett. 58, No. 9, March 1987, pp. 908-910).

With this development, integrated circuits cooled with liquid nitrogen, and in which both devices and connections consist of superconductor material, are expected to become reality provided high performance devices, e.g., effective switching elements, can be designed. The obstacles encountered in using hybrid semiconductor-superconductor techniques would be removed.

SUMMARY OF THE INVENTION

It is thus a primary object of the present invention to provide a high speed superconductor field-effect device that can be fabricated using the same technology as that used to produce the device connections and that can be operated as a switch at operating temperatures below the transition temperature T c of the superconductor material.

It is another object of this invention to provide a superconductor field-effect device that exhibits a large difference in channel current when switched between its ON and OFF states.

It is another object of this invention to provide a superconductive field-effect device that provides sufficient output signals to drive other such field effect devices.

The invention as claimed is intended to meet this objective and to remedy the drawbacks of hitherto known structures. It solves the task of providing a switch having a high ON/OFF current ratio in that the thickness of the superconductor channel is made sufficiently thin so that, when applying a control signal of

proper magnitude (a few Volts are sufficient) to the gate, the channel becomes completely depleted of charge carriers.

Accordingly, the device provides a high-performance switch element that is capable of switching from zero resistance (when superconducting) to "insulating" (when the channel is depleted). It also provides outputs sufficiently high to drive connected field-effect devices. Stringent operating temperature requirements are avoided because the operation does not rely on a "T c -shift" effect.

The device can be produced in the same high T c superconductor technology that is used in fabricating the integrated circuit wiring and device connections. That is, the same materials can be used for the interconnect elements as are used for the device channel.

Pat. No. 5401714, *

This field effect device utilizes a superconducting channel which is very thin and is comprised of a high T c superconductor, such as the oxide superconductors first described by Bednorz and Mueller. These superconductors have T c > 30o K., and include the known Y-based copper oxides with T c perspective to 90o K., Bi-based copper oxides with T c perspective to 115o K., and TI-based copper oxides with T c up to about 162o K. High T c superconductors which have small correlation lengths, enabling them to be made sufficiently thin that their carrier densities can be greatly altered substantially throughout their thicknesses by the application of electric fields of reasonable magnitude, are suitable.

The device also ...

... source and drain regions for providing an electric current along the high T c channel, and a gate region for providing the electric field that alters the carrier density of the high T c superconductor channel substantially throughout its thickness. The gate region is generally provided by a conductive material separated from the superconductor channel by an insulating region.

In operation, the channel remains at a temperature less than the superconductive transition temperature T c . When no electric field is applied, the maximum current from source to drain is the supercurrent through the channel (ON-STATE). When a sufficient electric field is applied across the channel, the carrier concentration ...

DETDESC:

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The inventive field-effect device comprises, in principle, the same basic elements as the surface effect superconductor FET structures that have previously been investigated and described, e.g., in the above-cited F. F. Fang et al article that was published in the IBM Technical Disclosure Bulletin.

Such a prior ad structure and its operation are illustrated in FIGS. 1A and

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1B. On an insulating or semi-insulating substrate 10, a superconductor channel 11 of about 10 nm thickness is deposited and provided with source 12 and drain 13 terminals. Gate 15 is separated from the channel by an insulating layer 14.

With properly chosen materials, at an operating ...

... T c of the channel material, and with no gate voltage (V g = 0) applied, the channel is "normal"-conducting thus providing, in the OFF-state of the device, a finite conductivity current path. It is however to be noted that, because the superconductors used are metals, the conductivity is high even in the OFF- or "normal conducting" state. In FIG. 1A, the resulting current is indicated by arrows 16. The current is equally distributed over the entire cross- ...

... zero voltage (V g not = 0) causes a slight change in carrier density within a thin surface layer 11a of a few tenths of a nanometer thickness near the superconductor-insulator interface. This change in carrier density results in an increase in T c within the very thin surface layer, to a value above the operating temperature T op of the device, thereby making the thin layer superconducting. In this ON-state, the device provides a current path of very

high conductivity. Arrow 17 represents the supercurrent flowing in the now superconducting layer 11a; there is no current flow in region 11b of the channel since it is shunted by the zero-resistance superconducting region 11a. The ON/OFF-current ratio is limited because, in the OFF-state, the normal-conducting channel is still conducting a rather heavy current. Also, the current-carrying capability of the very thin channel 11a is severely ...

... well as with a gate 25 that is separated from the channel by an insulating layer 24.

In a preferred embodiment, the substrate consists of strontium titanate (SrTiO3) on which the channel of a high-T c superconductor material, in the example YBa2Cu307, is grown. The channel is very thin, on the order of 1 nm, and is single crystalline and oriented so that the superconducting behavior is strongest in the plane parallel to the substrate surface.

For the growth of the thin channel layer an epitaxial process is used, followed by after-treatments such as oxygen anneal. Such techniques have more recently been ...

... 2. "Atomic Layer Epitaxy", H. Watanabe et al (Inst. Physics Conf. Ser. No. 83, Chapter 1, 1986, pp. 1-9).

MBE-grown high- T c superconductors have been described in, for example,

1. "Growth of high-T c Superconducting Thin Films using Molecular Beam Epitaxy Techniques" by C. Webb et al (Appl. Phys. Lett. 51, October 1987, pp. 1191-1193); and

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2. "Single Crystal Superconducting YBaCuO Oxide Films by Molecular Beam Epitaxy" by J. Kwo et al (Conf. Proceed. "Novel Mechanism of Superconductivity", June 22-26, 1987, Berkeley/US).

A suitable method for fabricating oriented layers using an evaporation process has been described by P. Chaudhari et al in an article entitled "Critical- ...

... layer can be applied in a vapor transport process such as chemical vapor deposition.

The gate 25 is then deposited on the insulator. In this preferred embodiment it is made of a high-T c superconductor, e.g. $YBa_2Cu_3O_7$, but any ordinary metal such as gold would work as well. Where a perovskite such as $SrTiO_3$ is used as insulator, the upper part of it could be made metallic either by using a reducing ambient or by doping with Nb so that a separate evaporation of a gate layer would not be required.

Source 23 and drain 24 leads can consist of the same material as the superconductor channel or of another high-T c superconductor. An ordinary metal may also be chosen.

Patterning of the structures can be done using conventional lithographic and/or etching methods.

Pat. No. 5401714, *

It should be noted that the ceramic superconductor materials such as the YBaCuO composition used in the described embodiment permit maximum current densities (above which the material becomes normal-conducting) of up to 10^{7} A/cm^{2} . The allowed channel ...

... channel thickness

For w = 10 mu and r = 1 nm, the calculated maximum current is 1 mA, i.e., an operating current level that is adequate for most applications.

It is furthermore noted that the use of the very thin superconductor channel, which is in the order of 1 nm, is feasible only because of the small coherent length of about 0.2 nm along the crystallographic c-axis that is achievable with the new class of metal-oxide superconductors such as the YBaCuO composition used in the embodiment. Since superconductivity can only subsist in layers having a thickness of at least the coherent length of the superconductor material, channels of a conventional metal superconductor such as lead or niobium, having coherent lengths that are at least an order of magnitude higher than that of the metal-oxide superconductors, would have to be much thicker. This then would prevent complete channel depletion with reasonable gate voltages, i.e., the device could not operate as a switch as will be described for the inventive FET structure in the following.

The operation of the superconductor FET will now be explained with the aid of

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FIGS. 3A and 3B. With no gate voltage V g applied (FIG. 3B), channel 21 is superconducting and the resistance between source 22 and drain 23 is zero. If a voltage is applied to gate 25 (FIG. 3A), the carrier concentration in the channel is changed due to the field effect. With a sufficiently high ...

... elemental charge

n = carrier density (10<21> /cm<3>)

t = thickness of insulating layer 24

on epsilon i , epsilon s , epsilon o = dielectric constants of insulating layer material, superconductor and air, respectively.

The required gate voltage can be fairly low (less than about 100 volts): with = 5 nm and d = 1 nm, the gate voltage V g required for ...

... voltage levels, for high outputs sufficient to drive connected FET devices. Use of the very thin (perspective to 1 nm) channel is feasible because

the correlation lengths of the metal-oxide class high-T c superconductors are sufficiently low (in the order of a few tenths of a nanometer),

these high-T c superconductors allow a high current density (10<7> A/cm<2>) that makes the device suitable for use in today's integrated circuits, and because

recently developed epitaxy techniques permit the growing of extremely thin layers (1 nm and less).

Pat. No. 5401714, *

When operated as a switch, the invention device does not rely on any T c -shift effect since there is no switching of the superconductor material between "superconducting" and "normal-conducting". Therefore, operating temperature requirements are not critical, allowing wide margins.

While the invention has been described with respect to particular embodiments thereof, it will be apparent to those of skill in the art that variations may be made therein without departing from the spirit and scope of the invention. For example, the geometry of the structure can be varied and complementary FET devices can be envisioned. By choosing high T c superconductors having small coherent lengths, the channel layer can be sufficiently thin that substantial depletion can occur substantially across the entire channel when voltage pulses of reasonable magnitude are applied to the gate. In particular, the high T c metal oxide superconductors, such as the copper oxide superconductors, are advantageous for the channel material. If voltage pulses of higher magnitude can be used, the channel layer can be thicker and/or superconductors with larger coherent lengths can be used while still obtaining a substantial carrier concentration change across the channel thickness.

What we claim as new and desire to secure by Letters Patent is:

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[*1] 1. A field-effect device with a channel having a superconducting property for use in electronic circuitry, the device comprising

a layer of superconductor material forming a channel through which a current of charge carriers may flow,

said channel has a charge carrier density and a length and a resistance,

a pair of terminals connected ...

... [*1] channel for applying an electric field to said channel in response to a control signal applied to the gate, the electric field affecting the charge carrier density within the channel and between the terminals,

wherein

said superconductor layer is sufficiently thin that, when applying said control signal of sufficient magnitude to said gate, substantially complete carrier depletion is achieved within said channel, switching the resistance of said channel from zero to insulating when said channel is depleted.

[*2] 2. The field-effect device of claim 1, wherein said channel is single crystalline and oriented so that the superconducting property is strongest in a plane parallel to the length of said channel.

[*3] 3. The field-effect device of claim 1, wherein said channel has a thickness of about 1 nm.

[*4] 4. The field-effect device of claim 1, wherein said superconductor material forming said channel has a transition temperature T_c that is higher than about 77 K.o.

[*5] 5. The field-effect device of claim 1, wherein said superconducting material has a crystallographic c-axis and wherein staid superconductor

material forming said channel has a coherent length of less than 0.5 nm along the crystallographic c-axis.

[*6] 6. The field-effect device of claim 1, wherein said superconductor material forming said channel has said charge carrier density of less than 10^{22} /cm^{3} .

[*7] 7. The field-effect device of claim 1, wherein said gate is separated from said channel by an ...

... [*10] field-effect device of claim 1, wherein the magnitude of the control signal required to cause complete carrier depletion in an entire cross-section of said channel is less than about ten volts.

[*11]   11. A superconductive field effect device, including

a layer of superconductive material forming a channel region through which electrical carriers can flow, said superconductive material being a metal oxide having a transition temperature greater than 77o K.,

source and drain means for providing said electrical carriers in said channel region,

said channel ...

... [*11]   channel is substantially completely depleted of carriers.

[*12]   12. The device of claim 11, where said channel has a thickness less than about a few nanometers.

[*13]   13. The device of claim 11, where the coherent length of said superconductive material is less than about 0.5 nm.

[*14]   14. The device of claim 11, where said superconductive material is a copper oxide.

[*15]   15. The device of claim 14, where said layer of copper oxide is a substantially epitaxial layer.

[*16]   16. The device of claim 11, where said gate means includes a conductive layer separated from said superconductive layer by an insulator, and means for applying a potential of less than about 10 volts to said conductive layer.

[*17]   17. A superconductive field effect device, comprising

a layer of superconductive material forming a channel region through which electrical carriers can flow, said superconductive material being a metal oxide layer having a transition temperature greater than 77o K., and a thickness less than about a few nanometers and having an electrical carrier density and a resistance,

source and ...

... [*18]   18. The device of claim 17, where said gate means includes a conductive layer to which a potential of less than 10 volts can be applied for producing an electric field in said superconductive channel having a magnitude sufficient to modulate said carrier density across substantially the entire thickness of said channel.

[*19]   19. The device of claim 18, where said superconductive material is a mixed copper oxide, there being an insulating layer between said conductive layer and said channel.

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[*20] 20. The device of claim 19, where said mixed copper oxide has a coherent length less than about 0.5 nm.

LEVEL 2 - 2 OF 2 PATENTS

4,997,809

<=2> GET 1st DRAWING SHEET OF 1

Mar. 5, 1991

Fabrication of patterned lines of high T c superconductors

INVENTOR: Gupta, Arunava, Valley Cottage, New York

T:
A method for producing a patterned layer of high T c oxide superconductor is provided in which patterning is accomplished prior to the attainment of a superconducting state in the layer. A solution containing precursor components of the desired oxide superconductor is sprayed onto a substrate and dried to provide a layer thereon. This layer is then irradiated in selected areas to convert the irradiated layers to an intermediate oxide state, the nonirradiated areas being unchanged. The nonirradiated areas are then dissolved away, leaving a pattern of oxide material. This oxide material is then converted to a high T c superconducting state, as by annealing in an oxygen atmosphere. This provides the patterned layer of high T c oxide superconductor. An example of a such a superconductor is a mixed copper oxide, such as Y1Ba2Cu3O 7-x .

SUM:

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to processes for producing patterned high T c superconducting layers, and more particularly to techniques that enable the writing of any type of pattern of high T c superconducting materials where the pattern is produced prior to the formation of a high T c superconducting phase in the materials.

2. Description of the Related Art

High T c oxide superconductors are materials of the type first discovered by J. G. Bendnorz and K. A. Mueller and reported by them in Z. Phys. B, 64, 189 (1986). These are superconducting oxides typically including combinations of 1 or more rare earth elements, alkaline earth elements, copper and oxygen and in which the transition temperature is greater than 30K. Typical high T c superconducting oxides are those fabricated from compounds of La, Sr, Cu and O, or Y, Ba, Cu and O. One of these materials, the Y-Ba-C-O oxide superconductor, has exhibited critical transition temperatures in excess of 77K. A particularly preferred single phase composition of this material is Y1Ba2Cu3O y , which is

often referred to as a "1-2-3" superconducting phase.

In the electronics industry, the fabrication of films of various thicknesses is important. In particular, the deposition of superconducting $YBa_2Cu_3O_{7-y}$ thin films has been obtained by various techniques, including sputtering, evaporation, and plasma spray coating. Related copending applications describing vapor transport and plasma spray coating of high T_c superconducting oxides

are Ser. No. 027,584, filed Mar. 18, 1987 and Ser. No. 043,523, filed Apr. 28, 1987, respectively. In addition, reference is made to the following technical journal articles which also describe the deposition of superconducting films.

1. R. B. Laibowitz et al, Phys. Rev. B, 35, 8821 (1987).

2. P. Chaudhari et al, Phys. Rev. Lett., 58, 2684 (1987).

3. ...

... et al, submitted to the American Ceramics Bulletin.

In thin film technology, it is necessary to provide patterns of the films when devices, interconnections, and packages are to be fabricated. In the case of high T_c oxide superconductors, it has become clear in the art that patterning of these materials is not trivial. Generally, the materials are ceramic copper materials having a perovskite-like structure that is not easily patterned. Wet photolithographic methods involve the use of various chemicals to which these ceramic materials are very sensitive, thus leading to alteration of their superconducting properties. Additionally, these materials tend to be porous and the use of chemicals will lead to etching of regions under an applied resist mask, thereby leading to poor resolution and undercutting.

Negative patterning of thin high T_c superconducting films can be done by ion lantation as described by G. C. Clark et al, Appl. Phys. Lett. 51, 139 (1987). This technique utilizes ions to destroy the superconductivity in the irradiated regions when the ion implantation is above a threshold dose. A superconducting quantum interference device (SQUID) was fabricated in this way and has been described by R. H. Koch et al in Appl. Phys. Lett. 51, 200 (1987). Additionally, this device and its fabrication technique are ...

... filed April 13, 1987, and assigned to the present assignee. The ion implantation technique is, however, limited to very thin layers of up to about 1-2 micrometers and also involves a high vacuum that tends to deplete oxygen from the superconducting film. Therefore, an annealing step is required after ion implantation. This may lead to diffusion of the implanted ions which could affect superconductivity in the film.

Another approach to patterning high T_c superconducting films is laser ablation using an appropriate mask either in contact with the film, or by projection imaging. This type of technique has been described by M. Scheuermann

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et al in an article submitted to Appl. ...

... ultraviolet wavelengths. This technique has limitations in that mask fabrication is required and the process itself produces debris which must in some way be removed.

In order to improve the patterning of layers of high T c superconductors, a discovery has been made which allows patterning to occur in a fabrication step prior to the achievement of a superconducting thin film. This inventive technique does not require the use of a mask and allows direct writing with an energy beam to accomplish patterning of any arbitrary geometry.

Accordingly, it is an object of this invention to provide an improved technique for producing patterns of high T c superconducting layers.

It is another object of this invention to provide a technique for patterning high T c superconducting layers which does not require that the layers be patterned after they are in a superconducting state.

It is another object of the present invention to provide a process that produces patterned high T c superconducting layers, where direct writing using an energy beam can be used to provide any desired pattern.

It is another object of the present invention to provide a technique for producing patterns of high T c superconducting layers, where the technique is not limited by the physical and chemical properties of the superconducting material.

SUMMARY OF THE INVENTION

This invention is a technique for providing patterned layers of high T c oxide superconductors. Rather than forming a layer of superconducting material and then patterning it, the present invention patterns a precursor layer before the layer is converted to a high T c superconducting state. This eliminates the disadvantages described hereinabove with respect to the difficulty of patterning these oxide superconductors.

In general, the steps of the process include the formation of a solution of the necessary constituents of the desired film in the proper proportions, the application of this solution to a substrate by a technique such as spraying, and the application of an ...

... a "development" step in that the nonirradiated portions are removed, as by dissolving them away in an appropriate solvent. The portions of the film which have been irradiated remain in this step. After this, the remaining oxide regions are made superconductive by annealing in an oxygen environment.

As an example, nitrates are prepared of the components that are to be present in the final superconducting film. These nitrates are mixed in the appropriate stoichiometric proportions and a solution of these nitrates is prepared. This

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solution is sprayed onto a substrate that is preferrably held at slightly elevated temperature. After the solvent has evaporated from the sprayed film,

...

... areas of the film are removed by dissolving them in a suitable alcohol solvent. The remaining patterned oxide film is then annealed at an appropriate temperature in an oxygen environment, and cooled to perfect the high T c superconducting state.

As will be apparent, any substrate can be used and the writing process can be accomplished by using an energy beam to either thermally or photochemically convert the irradiated regions to the desired oxide intermediate state. Additionally, the precursors can be other than nitrates, such as, for example, acetates. Any copper based high T c oxide superconductor can be provided as a patterned layer by this technique.

These and other objects, features, and advantages will be apparent from the following more particular description of the preferred embodiments.

DRWDESC:

BRIEF DESCRIPTION OF THE DRAWINGS

Pat. No. 4997809, *

FIGS. 1-4 schematically illustrate representative steps of the inventive process for providing patterned layers of high T c superconducting materials.

DETDESC:

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The general procedure in this process is the provision of a solution containing the constituents that are to be in the final high T c superconductor layer in their appropriate proportions, applying the solution as by spraying or spinning onto a substrate on which the layer is to be formed, applying an energy beam at localized regions of the layer to convert those irradiated regions to an intermediate oxide state, removing the nonirradiated portions, and perfecting the high T c superconducting state in the remaining oxide portions of the layer. These steps will be explained in more detail with reference to FIGS. 1A-1D, and examples will be given to illustrate further details of the process.

...

... solution which emanate from the airbrush 16. Although different examples of the solution will be described in more detail later, a representative example for ultimately providing a YBa2Cu3O 7 - x superconducting film can be a stoichiometric aqueous solution of nitrate precursors of Y, Ba, and Cu in the ratio Y:Ba:Cu = 1:2:3. This solution is sprayed onto the substrate 12, where the substrate is advantageously heated to ...

... Generally, water is not used for this developing step since, besides

removing the unirradiated nitrates effectively, it also tends to remove BaO from the irradiated regions, thereby affecting the stoichiometry which will be needed to provide a superconducting film. After irradiation and development, the regions 20 are highly insulating, rather than being conducting.

In FIG. 4, the patterned film-substrate combination is placed in a hot oven 24 (925o- ...

... shut off. Cooling is continued over a period of 2-3 hours down to about 200o C. and the sample is removed from the oven. In this state, the required stoichiometry for high T c superconductivity has been established and a pattern 20 of superconducting lines is then present on the substrate 12.

In this process, a film of the precursors was utilized to selectively change properties in the film so that a differential "development" step could be undertaken. After this, the remaining portions of the film were converted to a superconducting state. Thus, patterning is accomplished prior to the achievement of the superconducting state, in order to eliminate the difficulties encountered in trying to pattern superconductive materials of this type. Further, large area coatings can be achieved quickly and with minimal cost. These coatings can be provided over a wide thickness range, and the ultimate resolution of the patterned lines is ...

... epitaxially grown on the substrate with the c-axis perpendicular to the substrate surface, higher critical current densities will be achieved.

Any type of substrate can be used although, for YBa2Cu3O 7 - x superconducting films, the most suitable substrate appears to be yttria stabilized zirconia. Other substrates include, for example, SrTiO3, MgO, sapphire, etc.

While a laser beam is preferrable for the energy ...

... thermal effect is utilized. The decomposed film could be a mixed oxide or an intermediate phase.

The technique of this invention can be used to provide patterned films of all copper oxide based high T c superconductors. The precursor solution, while illustrated as a nitrate solution, can be a different type of solution, including an acetate, an acetylacetonate solution, or an alkoxide solution, etc. The nitrate precursor solution is advantageous in providing good control on the ratio of the elements that are to be in the superconductor film. Other examples are alkoxides and/or soaps (e.g., neodecanoate, napthenate, etc.) of these compounds which decompose at relatively low temperatures. By choosing the precursors carefully, the decomposition and anneal temperatures can be reduced significantly to allow the ...

... power is used to provide about 1-5 x 10<5 > W/cm<2> . If the laser power is too high the Ba stoichiometry in the converted oxide film is destroyed,

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making it difficult to achieve the superconducting state in films of YBaCu oxide. These upper limits will be varied by a small amount for other types of copper oxide superconducting films, such as the La-Ba-Cu-O and La-Sr-Cu-O compositions.

It is preferrable to initially use an solution, rather than a slurry (which is not as controllable) to provide a uniform thickness film. Further, a slurry may not be soluble and therefore not easily developed.

The following examples will illustrate the application of this process to the fabrication of patterned high T c superconducting films.

EXAMPLE I

In this example, a simple spray deposition technique is used to deposit a precursor film on a substrate. The ultimate goal is the preparation of patterned high T c superconducting thin films of $YBa_2Cu_3O_{7-x}$ on (100) single crystal MgO, ZrO_2 with 9% Y_2O_3 (yttria stabilized zirconia or YSZ) and $SrTiO_3$.

In a first step, a mixed nitrate powder of ...

... as well as others such as isopropanol. As noted, water could not be used for the development step.

The oxide lines which were left on the substrates were tested and found to be highly insulating, rather than superconducting. The patterned oxide film was then placed in a hot oven at 925o-950o C. under flowing helium for 5-20 minutes, after which the helium flow was replaced by a one ...

... in a heated environment was for about 1 minute. Cooling then continued for a period of 2-3 hours down to about 200o C. when the samples were removed from the oven and tested for superconductivity.

For lines written on MgO, superconducting oxides were produced having onset temperatures of about 82K. The completion, or the zero resistivity state occurred at a higher temperature for the blanket film than for the laser-written superconducting line. This is probably due to a higher reaction of the laser-written line with the substrate during irradiation and the possible removal of one or more of the components of the laser-written line in the development process. Another reason could ...

... annealing conditions which were not optimized. It was found that the Yttria stabilized zirconia substrates tended to provide films having higher temperature zero resistance states. For example, zero resistance states at 87K were measured for superconducting films formed on YSZ substrates. Other lines written on YSZ substrates showed an onset temperature of 92K and a completion of the superconducting transition at 85K.

EXAMPLE II

In this example, the various substrates are those described with respect to

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example 1. Patterns of $YBa_2Cu_3O_{7-x}$ superconducting films were formed using acetates as precursor solutions. Stoichiometric amounts of the powders of Y_2O_3, $BaCO_3$ and CuO were mixed with acetic acid and then evaporated to dryness to remove any excess acid. A dilute solution of 1- ...

... example 1.

It may be possible to vary the precursor solution somewhat to provide a sprayed film which can be directly converted by the energy beam into oxides of the appropriate stoichiometry to exhibit a superconducting state without the normally required annealing step. The provision of an oxygen environment during the beam writing step may provide sufficient amounts of oxygen in the irradiated regions that those regions will be superconducting after the irradiation step. This would allow one to accomplish patterning by development after energy beam writing, and would therefore be a low temperature process to achieve a patterned T c superconducting oxide layer. By eliminating the high temperature anneal, the fabrication of the patterned superconductor layer is more compatible with other processes in which lower preparation temperatures are desired.

In the practice of this invention, a film or layer is provided which is irradiated by an energy beam to create regions in the layer which are chemically and physically different than the unirradiated regions, thereby allowing a removal step that differentiates between the two regions in order to leave material which can be converted to a high T c superconducting state. In the course of this invention, the use of a technique such as spraying is preferable because of its ease of accomplishment and low cost, but it should be understood that other techniques can be utilized to produce the initial precursor ...

... skill in the art that variations can be made therein without departing from the spirit and scope of the present invention. Thus, the invention is directed to the provision of patterned films or layers of varying thickness of high T c oxide superconductors, and particularly those which are copper oxide based superconductors.

Having thus described our invention what we claim as new and desire to secure as Letters Patent, is:

Pat. No. 4997809, *

[*1] 1. A method for providing a patterned layer of high T c oxide superconductor material, comprising:

preparing a solution containing the components of said oxide superconductor in the proper stoichiometric ratios,

coating said solution onto a substrate to provide a coated layer thereon,

irradiating selected areas of said coated layer with an energy beam to convert said irradiated areas to an ...

... [*1] during conversion to an oxide state,

removing the nonirradiated areas of said coated layer to leave a patterned layer of said nonsuperconducting oxide, and

converting said patterned layer to a high T c superconducting state, thereby producing a patterned layer of high T c oxide superconductor.

[*2] 2. The method of claim 1, where said nonsuperconductive oxide is converted to a high T c superconducting state by annealing in an oxygen atmosphere.

[*3] 3. The method of claim 1, where said solution is coated on said substrate by spraying it thereon.

[*4] 4. The method of claim 1, where said patterned high T ...

... [*7] beam provides visible wavelengths.

[*8] 8. The method of claim 1, where said energy beam is scanned across said coated layer.

[*9] 9. The method of claim 1, where said high T c oxide superconductor is a mixed copper oxide.

[*10] 10. The method of claim 1, where said substrate is heated during said irradiation step.

[*11] 11. The method of claim 1, where said removing step is accomplished by dissolving said nonirradiated areas.

[*12] 12. A method for providing a patterned layer of high T c oxide superconductor material, comprising:

coating a substrate with a solution containing the components desired in said high T c oxide superconductor, said components being in solution in the proper ratios, and drying to provide a layer on said substrate,

locally converting selected areas of said layer to an oxide state while maintaining the cation components of said layer in the proper stoichiometric ratio,

removing nonselected areas of said layer to leave a patterned layer of oxide material, and

producing a high T c superconducting state in said patterned layer of oxide material.

[*13] 13. The method of claim 12, where said high T c superconducting state is YBa2Cu3O 7 - x .

[*14] 14. The method of claim 12, where said high T c superconducting oxide

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state is a mixed oxide of copper.

[*15] 15. A method for providing a patterned layer of oxide material that is a precursor to a high T c oxide superconductor, comprising the following steps:

preparing a solution containing the cation components of said high T c oxide superconductor, said cation components being in said solution in the proper stoichiometric amounts required in said high T c oxide superconductor,

coating said solution onto a substrate to produce a coated layer thereon,

irradiating selected areas of said coated layer with an energy beam to create regions having chemical properties different than those of the surrounding nonirradiated regions, ...

... [*15] stoichiometric amounts of said cation components, and

dissolving said nonirradiated regions to remove them from said layer, thereby leaving a patterned layer of oxide material which is a precursor to said high T c oxide superconductor.

[*16] 16. The method of claim 15, including the additional step of converting said patterned oxide precursor layer to a high T c superconducting state.

[*17] 17. The method of claim 16, where said high T c oxide superconductor is a mixed copper oxide.

[*18] 18. The method of claim 17, where said energy beam is a laser beam.

[*19] 19. The method of claim 15, where said solution is a nitrate solution.

[*20] 20. A method for providing a patterned layer of high T c copper oxide superconductor, comprising:

preparing a solution containing the components of said high T c oxide superconductor, said components being present in said solution in the amounts required in said high T c copper oxide superconductor,

spraying said solution onto a substrate to provide a coated layer thereon,

irradiating selected areas of said coated layer with an energy beam to convert said irradiated areas to an intermediate oxide state, the energy and ...

... [*20] areas of said coated layer to remove them, leaving a patterned layer of oxide material, and

annealing said patterned layer of oxide material in an oxygen atmosphere to

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produce a high T c superconductivity state, said oxide material being a copper oxide.

[*21] 21. The method of claim 20, where said substrate is heated during said spraying step and said irradiation step.

[*22] 22. The method of claim 21, where said energy beam is a laser beam.

[*23] 23. The method of claim 22, where said oxide superconductor is a Y-Ba-Cu-O oxide material.

[*24] 24. The method of claim 22, where said patterned high T c copper oxide superconductor is an epitaxial layer.

[*25] 25. A method for providing a patterned layer of high T c copper oxide s[illegible]rconductor material, comprising:

coating a substrate with a solution containing the components desired in said high T c copper oxide superconductor, said components being in solution in the proper ratios, to provide a layer on said substrate,

locally converting selected areas of said layer to an oxide state exhibiting high T c superconductivity by irradiating said selected areas with an energy beam whose energy fluence is less than that which would alter said proper ratios, and

removing nonselected areas of said layer to leave a patterned layer of high T c superconducting copper oxide material.

[*26] 26. The method of claim 25, where said removing step is achieved by dissolving away said nonselected areas.

[*27] 27. The method of claim 26, where said superconducting copper oxide [illegible]er is an epitaxial layer.

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